

NMR relaxation and resistivity from rattling phonons in pyrochlore superconductors

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We calculate the temperature dependence of NMR relaxation rate and electrical resistivity for coupling to a local, strongly anharmonic phonon mode. We argue that the two-phonon Raman process is dominating NMR relaxation. Due to the strong anharmonicity of the phonon an unusual temperature dependence is found having a low temperature peak and becoming constant towards higher temperatures. The electrical resistivity is found to vary like T^2 at low temperatures and following a \sqrt{T} behavior at high temperatures. Both results are in qualitative agreement with recent observations on β -pyrochlore oxide superconductors.

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The recent discovery of superconductivity in the family of pyrochlore oxides KOs_2O_6 , RbOs_2O_6 , and CsOs_2O_6 has attracted great interest because of their unusual properties. Among these KOs_2O_6 with the highest T_c of 9.6 K appears to be the most unusual. The temperature dependence of its electrical resistivity shows a strong concave-downward temperature dependence [1, 2], in contrast to the other two compounds, where a T^2 temperature dependence at low temperatures has been observed [3, 4]. Specific heat measurements have shown a large mass enhancement, large specific heat jump at T_c , and existence of low frequency Einstein modes [5, 6]. Band-structure calculations have indicated that the anomalies, in particular in KOs_2O_6 , might be due to a highly anharmonic low frequency rattling motion of the alkali-ion inside an oversized cage formed by the Os and O ions [7, 8]. This is consistent with X-ray observations of anomalously large atomic displacements for the K ions [9] and low frequency phonon structures seen in photoemission spectroscopy [10].

Recent observations of NMR relaxation rates $1/T_1T$ at the K site have been demonstrated to be entirely dominated by the vibrations of the K ion via coupling of the electric field gradient to the nuclear quadrupole moment [11]. Such a domination of phonons for nuclear relaxation usually occurs in diamagnetic insulators, but is extremely rare in metals and was attributed to the rattling motion of the K ions. The temperature dependence of $1/T_1T$ was found to be anomalous as well, showing a peak around 12-14 K and decreasing at higher temperatures. It has been argued that such a behavior is inconsistent with the two-phonon Raman process, which usually dominates quadrupolar relaxation, and it has been interpreted in terms of the direct phonon process with a strongly temperature dependent phonon damping rate [11]. In the superconducting state $1/T_1T$ exhibits a sudden decrease, suggesting a strong coupling of the phonon mode to the conduction electrons and an associated increase of the phonon lifetime in the superconducting state.

Motivated by these experimental findings, in the present work we study the influence of a local, strongly anharmonic, and damped phonon mode on the NMR relaxation rate and the electrical resistivity. We find that within this model the two-phonon Raman process is expected to dominate NMR relaxation over the direct process. Due to the anharmonicity of the phonon mode the temperature dependence of $1/T_1T$ for the Raman process is qualitatively different from harmonic phonons. We show that the experimental data are qualitatively reproduced, showing a peak at about half the low temperature phonon frequency and decreasing towards a constant value at higher temperatures. Within the same model also the temperature dependence of the resistivity can be understood, following a T^2 law at low temperatures and a \sqrt{T} behavior at high temperature. Thus, a qualitative understanding of both the anomalous NMR relaxation and electrical resistivity can be obtained simultaneously by considering the anharmonicity of the phonon involved.

As a description of the local alkali-ion motion we start from an anharmonic Hamiltonian of the form

$$H = \frac{p^2}{2M} + \frac{1}{2}ax^2 + \frac{1}{4}bx^4 \quad (1)$$

where x , p , and M are the spacial coordinate, momentum, and mass of the alkali-ion, respectively, and a and $b > 0$ are constants. We note that according to band-structure calculations, in KOs_2O_6 the quadratic term even becomes negative $a < 0$, resulting in a shallow double well potential, while in the other two compounds a is positive [7]. We treat this Hamiltonian in a selfconsistent quasi-harmonic approximation resulting in an effective harmonic Hamiltonian

$$H = \frac{p^2}{2M} + \frac{1}{2}M\omega_0^2x^2 \quad (2)$$

where the effective phonon frequency ω_0 becomes temperature dependent and has to be determined selfconsistently from the equation $M\omega_0^2 = a + b\langle x^2 \rangle_{\omega_0, T}$. Here,

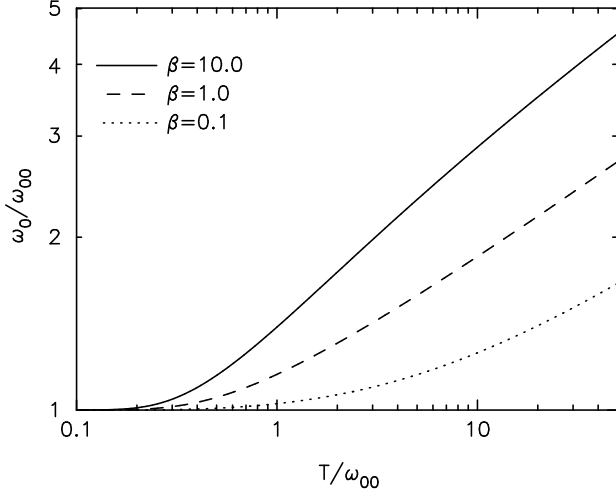


FIG. 1: Effective phonon frequency ω_0/ω_{00} as a function of temperature T/ω_{00} for anharmonicity parameter $\beta = 0.1, 1$, and 10 (double logarithmic scale).

$\langle x^2 \rangle_{\omega_0, T}$ denotes the thermal average of x^2 that depends on both ω_0 and temperature T and is given by

$$\langle x^2 \rangle_{\omega_0, T} = \frac{\hbar}{M\omega_0} \left[\frac{1}{e^{\hbar\omega_0/k_B T} - 1} + \frac{1}{2} \right]. \quad (3)$$

Note, that the effective phonon frequency ω_0 is a thermodynamical average frequency and not to be confused with the discrete, temperature independent energy levels of the Hamiltonian Eq. (1). In the zero temperature limit we have

$$\omega_0^2(T=0) = \frac{a}{M} + b \frac{\hbar}{2M^2\omega_0(T=0)} \quad (4)$$

Note that this equation guarantees $\omega_0(T=0) > 0$ for $b > 0$, even if $a < 0$. In the high temperature limit $T \gg \omega_0$ we find

$$\omega_0 \sim \left(\frac{bk_B T}{M^2} \right)^{1/4}. \quad (5)$$

We can eliminate the parameter a in favor of $\omega_{00} = \omega_0(T=0)$ using Eq. (4). Then we can derive the following nonlinear equation:

$$\left(\frac{\omega_0}{\omega_{00}} \right)^2 = 1 + \beta \frac{\omega_{00}}{\omega_0} \left[\frac{1}{e^{\hbar\omega_0/k_B T} - 1} + \frac{1}{2} - \frac{1}{2} \frac{\omega_0}{\omega_{00}} \right] \quad (6)$$

where $\beta = b \frac{\hbar}{M^2\omega_{00}^3} > 0$ is a dimensionless parameter characterizing the amount of anharmonicity. In Fig. 1 $\frac{\omega_0}{\omega_{00}}$ is shown as a function of T/ω_{00} for $\beta = 0.1, 1$, and 10 . $\frac{\omega_0}{\omega_{00}}$ is a monotonously increasing function of temperature.

Defining the retarded phonon propagator as

$$D(\omega) = -i \frac{2\omega_0 M}{\hbar} \int_0^\infty dt e^{i\omega t} \langle [x(t), x(0)] \rangle \quad (7)$$

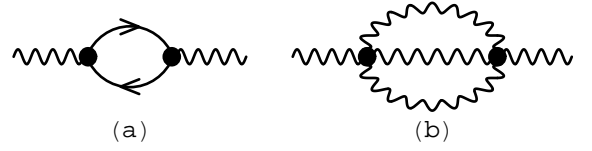


FIG. 2: Two lowest order processes leading to a finite phonon lifetime: (a) coupling of the phonon to the conduction electrons and (b) fourth order phonon process due to the anharmonicity.

the interaction of the phonon with the conduction electrons can be described by the phonon self-energy $\Pi(\omega)$ via Dyson's equation $D^{-1}(\omega) = D_0^{-1}(\omega) - \Pi(\omega)$. Here, the noninteracting phonon propagator due to the effective Hamiltonian Eq. (2) is given by $D_0(\omega) = \frac{2\omega_0}{\omega^2 - \omega_0^2}$. Thus, the phonon propagator can be written in terms of the self-energy as

$$D(\omega) = \frac{2\omega_0}{\omega^2 - \omega_0^2 - 2\omega_0\Pi(\omega)} \quad (8)$$

The real part of the self-energy leads to a renormalization of the phonon frequency $\omega_r^2 = \omega_0^2 + 2\omega_0 \text{Re } \Pi(\omega)$ while the imaginary part determines the damping width $\Gamma(\omega) = -\text{Im } \Pi(\omega)$. Due to symmetry the damping width has to be an odd function $\Gamma(\omega) = -\Gamma(-\omega)$, while the real part has to be even $\text{Re } \Pi(\omega) = \text{Re } \Pi(-\omega)$. In Fig. 2 we show the two lowest order processes contributing to a finite phonon damping. Process (b) is due to the fourth order process neglected in Eq. (2). This process does not lead to a change of the phonon damping, when superconductivity sets in. As mentioned above, the NMR results suggest that there is a strong coupling of the phonon to the conduction electrons and therefore we expect process (a) to play the leading role. Since the Fermi energy of the conduction electrons is a much larger energy scale than the phonon energies, process (a) will be featureless in the low energy range of interest in the normal state. The damping width is a linear function at low energy and we can write $\Gamma(\omega) = \alpha\omega$. The real part of the self-energy can be assumed constant and must be negative (i.e. the electron-phonon interaction leads to a softening of the phonon). The dimensionless parameter α determines the phonon damping and is given by $\alpha = g^2 N^2(0)$, where $N(0)$ is the density of states at the Fermi level and g the electron-phonon coupling constant. It is important to keep in mind that $g^2 \sim \omega_0^{-1}$, because here ω_0 is temperature dependent. Therefore, in the following we write $\alpha = \Gamma_0/\omega_0$, where Γ_0 is a (temperature independent) phonon damping rate and will be treated as a phenomenological parameter. The phonon spectral function is given by

$$A(\omega) = -\frac{1}{\pi} \text{Im } D(\omega) = \frac{1}{\pi} \frac{4\omega_0 \Gamma_0 \omega}{(\omega^2 - \omega_r^2)^2 + 4\Gamma_0^2 \omega^2} \quad (9)$$

This is equivalent to the familiar damped harmonic oscillator formula apart from the fact that ω_r becomes temperature dependent here due to the anharmonicity.

The quadrupolar NMR relaxation rate is usually dominated by the two phonon Raman process [12], which is given by

$$\frac{1}{T_1^R} = V_2^2 \int_{-\infty}^{\infty} dt e^{i\omega_L t} \langle x^2(t) x^2(0) \rangle \quad (10)$$

where V_2 is proportional to the second spacial derivative of the electric field gradient and ω_L is the nuclear Larmor frequency, which is usually very small. In Ref. 11 it has been suggested, however, that in the case of KOs_2O_6 the direct (one phonon) process might be dominating instead. Here, we are comparing these two processes for our model. For the direct process we have

$$\frac{1}{T_1^D} = V_1^2 \int_{-\infty}^{\infty} dt e^{i\omega_L t} \langle x(t) x(0) \rangle \quad (11)$$

where V_1 is proportional to the first spacial derivative of the electric field gradient. Using the fluctuation-dissipation theorem we can directly relate $\frac{1}{T_1^D}$ to the phonon spectral function: $\frac{1}{T_1^D} = 2\pi V_1^2 \frac{\hbar}{2\omega_0 M} \frac{1}{1 - e^{-\hbar\omega_L/k_B T}} A(\omega_L)$. Assuming $\hbar\omega_L \ll k_B T$ we find

$$\frac{1}{T_1^D T} = 2\pi V_1^2 \frac{k_B}{2\omega_0 M} \lim_{\omega \rightarrow 0} \frac{A(\omega)}{\omega} = 2V_1^2 \frac{k_B}{2\omega_0 M} \frac{4\omega_0 \Gamma_0}{\omega_r^4} \quad (12)$$

As has been pointed out in Ref. 11, this expression is monotonously decreasing as a function of temperature and thus cannot reproduce the observed peak in $\frac{1}{T_1 T}$. Due to the temperature dependence of ω_0 at high temperatures we have $\frac{1}{T_1^D T} \sim \omega_0^{-4} \sim T^{-1}$.

Following the discussion of the Raman process in Ref. 12 we can also express Eq. (10) in terms of the phonon spectral function:

$$\frac{1}{T_1^R} = 2\pi \left(\frac{\hbar}{2\omega_0 M} \right)^2 V_2^2 \int_{-\infty}^{\infty} d\omega A^2(\omega) [n(\omega) + 1] n(\omega) \quad (13)$$

At sufficiently high temperatures $T \gg \omega_r$, in the normal state we can approximate the Bose function $n(\omega) \approx \frac{k_B T}{\hbar\omega}$ and Eq. (13) can be evaluated analytically. After some algebra we arrive at

$$\frac{1}{T_1^R} = \left(\frac{k_B T V_2}{2\omega_0 M} \right)^2 \frac{2\omega_0^2}{\Gamma_0} \frac{4\Gamma_0^2 + \omega_r^2}{\omega_r^6} \quad (14)$$

Due to the temperature dependence of ω_0 in Eq. (5) we find the high temperature behavior

$$\frac{1}{T_1^R T} \sim T \omega_0^{-4} \sim \text{const} \quad (15)$$

Thus, $\frac{1}{T_1^R T}$ approaches a constant high temperature value for anharmonic phonons. This is in strong contrast to

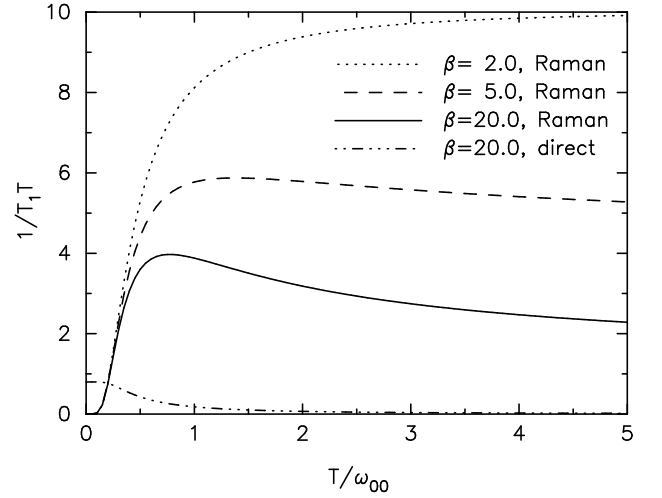


FIG. 3: Temperature dependence of $1/T_1 T$ for the Raman process and anharmonicity parameter $\beta = 2$ (dotted), 5 (dashed), and 20 (solid). The dashed-dotted line shows the direct process for comparison.

harmonic phonons, where $\frac{1}{T_1^D T}$ is increasing linearly with T . To estimate the relative importance of the two processes we can use Eqs. (14) and (12) to calculate the ratio

$$\frac{T_1^D}{T_1^R} = \frac{V_2^2}{V_1^2} \frac{k_B}{2\omega_0 M} \frac{4\Gamma_0^2 + \omega_r^2}{\omega_r^2} \frac{T\omega_0}{4\Gamma_0^2} \quad (16)$$

From this expression it becomes clear that the Raman process is certainly dominating at high temperature and also, when the phonon damping Γ_0 is small. We note that the ratio $\frac{V_2}{V_1}$ has dimension of an inverse length, which should be of the order of magnitude of the size of the potential, in which the K ion moves. Therefore, as an order of magnitude estimate we assume $\frac{V_2^2}{V_1^2} \frac{\hbar}{2\omega_0 M} \sim 1$.

In the normal state at low enough temperatures Eq. (13) leads to

$$\frac{1}{T_1^R T} \sim T^2 \quad (17)$$

because of the linear ω dependence of $A(\omega)$. As an illustration Fig. 3 shows a numerical calculation of $\frac{1}{T_1^R T}$ as a function of T/ω_{00} based on Eqs. (13) and (6) for $\Gamma_0/\omega_{00} = 0.1$, $\text{Re } \Pi = 0$, and three different values for the anharmonicity parameter $\beta = 2, 5$, and 20. Clearly, with increasing anharmonicity a low temperature peak develops near $T \approx \omega_{00}/2$ and becomes more pronounced. This can be understood from the ω_0^{-4} behavior in Eq. (15): at low temperatures ω_0 becomes constant and all curves fall on top of each other. However, at higher temperatures ω_0 increases the stronger the larger β is, resulting in a quick decrease for larger β . For comparison, the dashed-dotted line shows the direct process for $\beta = 20$, assuming $\frac{V_2^2}{V_1^2} \frac{\hbar}{2\omega_{00} M} = 1$. Clearly, the direct process can be neglected over most of the temperature range. We mention

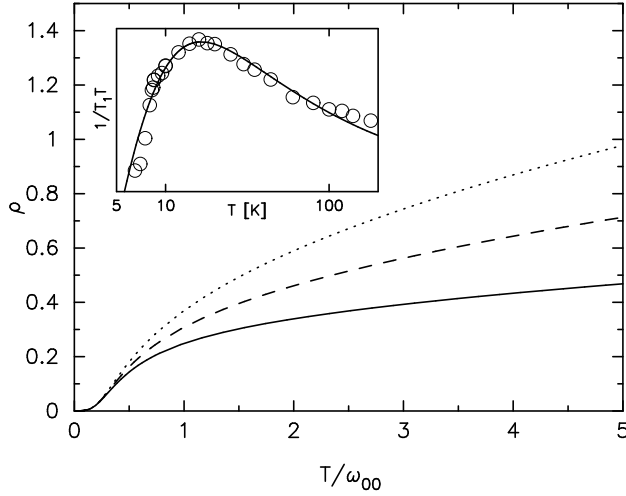


FIG. 4: Temperature dependence of the resistivity for the same parameters as in Fig. 3. Inset: Temperature dependence of $1/T_1T$ fitted to the experimental data of Ref. 11 (sample A) on a double logarithmic scale.

that the direct process is exponentially suppressed in the superconducting state.

In the inset of Fig. 4 we show a fitting of Eq. (13) to the experimental data of Ref. 11 (sample A). From this fit the following parameters are found: $\omega_r(T=0) = 27.4$ K, $\beta = 6.27$, $\Gamma_0 = 4.0$ K, and $\omega_0 \text{Re } \Pi = -(21 \text{ K})^2$. The low temperature value of the renormalized phonon frequency $\omega_r(T=0) = 27.4$ K is in reasonable agreement with a low frequency Einstein frequency of 22 K found in fits to specific heat data [6] and 24.4 K found from a phonon structure in photoemission [10].

In the following we calculate the resistivity due to coupling to the local anharmonic phonon Eq. (9). We will follow the work by Mahan and Sofo [13]. The imaginary part of the retarded electronic self energy is given by

$$-\text{Im } \Sigma(E) = \tau^{-1}(E) = \pi g^2 N(0) \int_0^\infty d\Omega A(\Omega) [2n(\Omega) + f(\Omega + E) + f(\Omega - E)] \quad (18)$$

where $f(\Omega) = \frac{1}{e^{\hbar\omega/k_B T} + 1}$ is the Fermi function. The resistivity can be calculated from $\rho(T) = \frac{4\pi}{\omega_p^2} \frac{1}{\tau(T)}$ where ω_p is the Plasma frequency and the electronic lifetime is given by $\tau(T) = -\int_{-\infty}^\infty dE \tau(E) \frac{df}{dE}$. We note that we can neglect vertex corrections here, because the phonon is local, i.e. momentum independent. Therefore, the transport lifetime is the same as the electronic lifetime.

Because $A(\Omega)$ is linear in Ω at low frequencies, we find from Eq. (18) that at temperatures $T \ll \omega_r$ the resistivity varies like $\rho \sim T^2$. However, in the high temperature limit we find from Eq. (18):

$$\tau^{-1} = 2\pi T g^2 N(0) \int_0^\infty d\Omega \frac{A(\Omega)}{\Omega} = 2\pi T \frac{\Gamma_0}{N(0)\omega_r^2} \quad (19)$$

Therefore, at high temperatures the resistivity varies as $\rho \sim \sqrt{T}$, a concave-downward temperature dependence. In Fig. 4 numerical results for the resistivity ρ are shown for the same parameters as in Fig. 3. With increasing β the concave-downward temperature dependence becomes more pronounced. Considering $\omega_{00} \sim 25$ K this result is in qualitative agreement with the resistivity data on KOs_2O_6 [2, 6]. A quantitative fitting would require taking into account the other, harmonic phonon modes as well. Since at present not much is known about these a more quantitative comparison has to await more detailed experimental information.

In conclusion, we have calculated the temperature dependence of NMR relaxation rates and resistivity due to coupling to a strongly anharmonic phonon mode. Our results are in agreement with recent experiments on β -pyrochlore superconductors, where such an anharmonic rattling motion of the alkali-ions is believed to cause various anomalies. Our theory may also be applicable to other rattling systems like the filled skutterudite $\text{LaOs}_4\text{Sb}_{12}$, as a recent NMR study suggests [14].

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